

Substituent Effects in the ^{13}C NMR Chemical Shifts of *Para*-(*para*-substituted benzylidene amino)benzonitrile and *Para*-(*ortho*-substituted benzylidene amino)benzonitrile

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^{13}C NMR chemical shifts were measured in CDCl_3 for two series of substituted benzylidene anilines. The substituted benzylidene anilines $p\text{-X-C}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{-}p\text{-CN}$ $p\text{-X-C}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{-}o\text{-CN}$ ($\text{X} = \text{NO}_2, \text{F}, \text{Cl}, \text{Br}, \text{H}, \text{Me}, \text{MeO}, \text{NMe}_2$). The substituent dependence of $\delta_{\text{C}}(\text{C}=\text{N})$ was used as a tool to study electronic substituent effects on the azomethine unit. The benzylidene substituents X have a reverse effect on $\delta_{\text{C}}(\text{C}=\text{N})$: electron-withdrawing substituents cause shielding, while electron-donating ones do the reverse, the resonance effects clearly predominating over the inductive effects. Additionally, the presence of a specific cross-interaction between X and C=N could be verified. The electronic effects of the neighboring aromatic ring substituents systematically modify the sensitivity of the C=N group to the electronic effects of the benzylidene substituents. These results can be rationalized in terms of the substituent-sensitive balance of the electron delocalization (mesomeric effects).

Keywords: N-Benzylideneaniline, Substituent effects, DSP analysis, Reynolds' model

INTRODUCTION

Several studies have been reported on the effects of substituents on NMR spectra of N-benzylideneanilines, which throw some light on the transmission of electronic effects within these molecules. The liquid-crystal and nonlinear optical properties of organic molecules with conjugated π -electron systems carrying an electron acceptor group at one end and a donor group at the opposite end have led to increasing interest in their properties. For example, both substituted phenyl benzoates and substituted benzylidene anilines are models of the molecular cores of mesogens, *i.e.*, compounds able to form liquid crystals [1,2]. These

compounds are of the general type $\text{X-C}_6\text{H}_4\text{-Z-C}_6\text{H}_4\text{-Y}$, where Z functions as a linking unit between two aromatic rings carrying the substituents X and Y which can act as electron donors and/or electron acceptors. The optical and electrical properties of liquid crystals have been shown to be sensitive to subtle changes in the structure of the molecule [1-6]. Changes in the substituents X and Y affect the overall electron distribution of $\text{X-C}_6\text{H}_4\text{-Z-C}_6\text{H}_4\text{-Y}$ and consequently the conformation of the molecule. An understanding of the mechanisms of charge generation at a molecular level is vital for an understanding of charge generation, transport, and trapping in photorefractive liquid crystals and for the design of new materials for nonlinear optical purposes.

Although NMR shielding is not determined only by the electron density, linear correlations with positive slopes between the atomic charges and the ^{13}C NMR chemical shifts

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to probe nuclei have been observed in several systems when the substitution is varied [7-14]. Good correlations have also been observed between the chemical shifts of the unsaturated carbons in the side chains of aromatic rings and substituent parameters [7,8,12,15-17]. Although the shift data do not usually fit the single-parameter correlation (Eq. 1), good to excellent correlations have been obtained with Eq. (2),

$$\text{SCS} = \rho\sigma \quad (1)$$

$$\text{SCS} = \rho_F\sigma_F + \rho_R\sigma_R^\circ \quad (2)$$

where SCS (substituent-induced change in the chemical shift) is the ^{13}C NMR shift of the side-chain carbon for a substituted compound relative to that for the unsubstituted one, and σ_F and σ_R° are the inductive and resonance parameters, respectively, for the aromatic ring substituent in question.

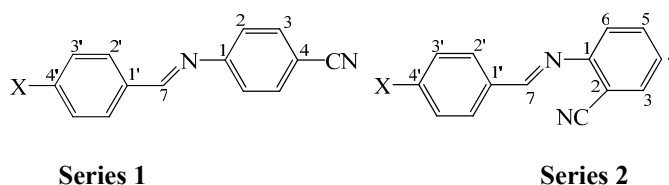
In this study, we investigated the correlation analysis of carbon-13 chemical shifts of C-7 for two series of substituted *N*-benzylideneaniline derivatives (Fig. 1) by applying Reynolds' Model. ^{13}C NMR data were reported for C-1', C-7, C-1, and the C \equiv N carbons at reasonably low concentration [18].

RESULTS AND DISCUSSION

Our main goals were to study the effect of the aniline substituent on the sensitivity of the electronic properties of the C=N group to the benzylidene substituent and the effect of the benzylidene substituent on the sensitivity of the electronic properties of the imine bridging group to the aniline substituent. We investigated the effects of the benzylidene substituents on $\delta_{\text{C}}(\text{C}=\text{N})$.

The ^{13}C NMR spectra of the benzylidene anilines shown in Fig. 1 are listed in Table 1.

Both electron-withdrawing (EW) and electron-donating (ED) benzylidene substituents cause shielding of the C=N carbon as compared with the unsubstituted derivative X =H (Table 1). This is despite the general idea that ED substituents cause shielding while EW substituents cause deshielding. However, analogous findings have been observed previously for the azomethine carbon of substituted benzaldehyde derivatives [8,12,19-26]. The $\delta_{\text{C}}(\text{C}=\text{N})$ values were first



X: H, N(CH₃)₂, OCH₃, CH₃, Cl, NO₂, Br, F

Fig. 1

correlated with the Hammett σ values according to Eq. (1). The results proved to be good for series 1 and poor for the series 2 as shown in Eqs. (3) and (4), respectively.

$$\text{SCS} = -1.64 \sigma_p^\circ \quad (3)$$

$$n = 8, r = 0.905, S = 0.41$$

$$\text{SCS} = -1.64 \sigma_p^\circ \quad (4)$$

$$n = 8, r = 0.853, S = 0.53$$

where n is the number of compounds, r is the correlation coefficient, and S is the standard deviation.

It is interesting to note that, according to Table 1, the C-nitrile shifts for compounds 2 are shielded by about 2 ppm compared with the CN shifts in compounds 1. It is also interesting to ask why C-7 is shielded in Compounds 1 compared with the same shifts in compounds 2. This may be due to the interaction which occurs between the nitrile group in the ortho position (Series 2) and H of azomethine, as well as, the effect of being in a resonance position just beside nitrogen (high deshielding) is counterbalanced by the fact that resonance decreases the double bond character of the azomethine function, which in turn, decreases the anisotropy of such a bond, thus causing a shielding effect [27]. This phenomenon needed further study, and was thus postponed for the time being.

However, good to excellent correlations were observed when the dual substituent parameter approach (Eq. 2) was used (Reynolds' Model). For two series, the correlation parameter ρ_F was quite small and negative, while the correlation parameter ρ_R was large and negative in series 1 and 2. In other words, resonance effects predominate strongly. The negative sign of the correlation parameters means a reverse substituent effect; *i.e.*, EW substituents cause shielding, while

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Table 1. ^{13}C NMR Chemical Shifts of 4-(4-Substitutedbenzylideneamino) Benzonitrile (Series 1) and 2-(4-Substitutedbenzylideneamino)benzonitrile (Series 2)


Series	Sub.	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	C-7	C-Nitryl	Others
1a	H	156.0	121.6	133.3	109.1	-	-	135.5	129.2	128.9	132.2	162.3	119.0	-
2a		154.6	107.3	133.2	125.8	133.8	119.2	135.4	129.5	128.9	132.4	163.1	117.3	-
1b	(NCH ₃) ₂	157.0	121.7	133.1	107.8	-	-	123.6	131.0	111.5	153.0	161.8	119.3	40.0
2b		155.7	107.3	133.2	124.7	133.5	119.3	123.6	131.3	111.4	153.1	162.2	117.7	40.1
1c	OCH ₃	156.3	121.6	133.2	108.6	-	-	128.6	131.1	114.4	163.0	161.5	119.1	55.5
2c		155.0	107.2	133.0	125.7	133.5	119.4	128.7	131.5	114.2	163.3	162.3	117.8	55.5
1d	CH ₃	156.1	121.6	133.2	108.7	-	-	133.0	129.2	129.6	142.9	162.2	119.0	21.7
2d		155.0	107.4	133.4	125.8	134.0	119.5	133.0	129.5	129.9	143.3	163.0	117.4	21.5
1e	Cl	155.6	121.6	133.4	109.4	-	-	134.1	130.4	129.3	138.4	160.8	118.9	-
2e		154.0	107.4	133.2	126.0	133.8	118.9	133.8	130.5	129.1	138.4	161.4	117.2	-
1f	Br	155.5	121.5	133.4	109.4	-	-	134.4	130.5	132.6	127.0	161.0	118.9	-
2f		153.9	107.4	133.2	126.1	133.7	118.9	134.2	130.7	132.1	127.0	161.5	117.2	-
1h	NO ₂	154.9	121.6	133.5	110.2	-	-	140.7	129.9	124.1	149.9	159.8	118.7	-
2h		153.7	107.7	133.5	126.9	133.9	118.9	140.6	130.1	124.1	149.8	160.4	118.0	-

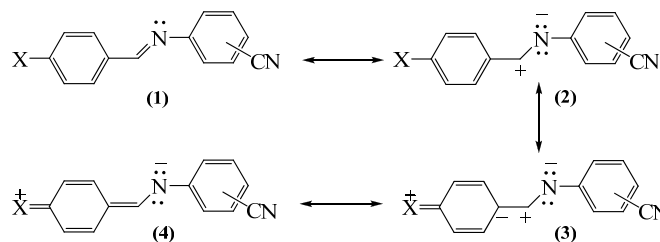
ED ones cause deshielding.

$$\text{SCS} = -0.03 - 0.06 \sigma_F - 3.43 \sigma_R^0 \quad (5)$$

$n = 8, r = 0.978, S = 0.22$

$$\text{SCS} = 0.02 - 0.29 \sigma_F - 3.75 \sigma_R^0 \quad (6)$$

$n = 8, r = 0.978, S = 0.22$



Scheme 2

The ^{13}C NMR chemical shift behavior described above can be explained by considering the resonance structures shown in Scheme 2. ED substituents X inductively stabilize resonance structure **2**, while EW ones have an opposite effect. The increase in the contribution of **2** caused by ED substituents affects the deshielding of the C=N carbon, with a negative value of $\rho_F(X)$ as the result. Substituents capable of ED

resonance as in **4** affect the deshielding of the imine carbon. The negative $\rho_R(X)$ values reflect the contribution of this resonance-promoted inductive effect. This explanation is supported by our previous study concerning substituent dependence of the ^{15}N NMR chemical shift of the C=N

nitrogen of substituted benzylidene anilines *p*-XC₆H₄CH=NC₆H₅ [8].

CONCLUSIONS

The benzylidene substituents in series 1 and 2 have been shown to have a systematic electronic effect on the shielding of the imine carbon in the substituted benzylidene anilines. The benzylidene substituents display an effect opposite to the normal one. The variations in the donor and acceptor properties of the benzylidene substituents lead to characteristic changes in the polarity of the C=N group. The resonance effects of the substituents on the benzylidene ring predominate over the inductive effects.

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